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6. AUTHOR(S) Karen L. Wooley			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Washington University, Department of Chemistry One Brookings Drive, CB 1134 St. Louis, MO 63130-4899		8. PERFORMING ORGANIZATION REPORT NUMBER	
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13. ABSTRACT (Maximum 200 words)  Macromolecular structures of varying architectures have been prepared and studied, in order to gain a fundamental understanding of the role of molecular parameters upon the properties of polymeric materials and to lead to the development of unique and advanced materials. Improved knowledge of the structural conformation, three-dimensional solid-state packing, and physical and mechanical properties of highly-branched polymers has been gathered through several means of investigation, each involving the study of fluorine-containing dendritic or hyperbranched polymers. Dendritic (tree-like) macromolecules have been shown by several research groups to possess very interesting behavior, due to a three-dimensional globular shape, branched architecture and large number of chain end functionalities. By placing a fluorine atom at the focal point of the globular dendritic molecule, we have quantitatively determined the intramolecular location of the chain end groups relative to the remainder of the structure as being distributed throughout the internal and external regions, and have characterized the nature of intermolecular packing in the solid state. The micromechanical properties of ultra-thin film samples of dendritic macromolecules have been measured by atomic force microscopy, and comparisons have been made with linear polymers of exact compositional equivalence. This research then inspired the study of dendritic and hyperbranched polymers, which contained a high level of fluorocarbon groups to impart low surface energies and create minimally-interacting nanoscale globular molecules. Surface energies and adhesive forces lower than those for PTFE were accomplished, and these materials showed superior performance in applications such as mold release agents.			
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**1) List of Illustrations and Tables.**

**Figure 1.** A fifth generation benzyl ether dendrimer, illustrating the chemical structure and the  $^{13}\text{C}$  and  $^{19}\text{F}$  labeling.

**Figure 2.** Molecular model of a cluster of seven fifth generation benzyl ether dendrimers, which was generated using the REDOR solid-state NMR data for intermolecular  $^{13}\text{C}$  (chain end) to  $^{19}\text{F}$  (focal point) distances.

**Figure 3.** AFM experiments reveal that the dendrimers are machined at low forces, due to the lack of intermolecular entanglements. In contrast, the linear polymer analogs (same composition and molecular weight, but 0% branching) develop periodic oscillatory patterns under the force of the scanning probe tip, resulting from stick-slip behavior that is characteristic of entangled polymer chains. These differences in behavior are expected to have implications toward the solid-state applications of dendritic materials.

**Figure 4.** Polymerization of the A2B monomer to yield the hyperbranched fluoropolymer. Subsequent chain end reactions allow for modification of the chain end compositions.

**Figure 5.** Intermolecular reactions produce the hyperbranched fluoropolymer (Acyclic HBFP), whereas a combination of intermolecular reactions with an intramolecular cyclization yields the cyclic HBFP. Each of the acyclic and cyclic materials at differing degrees of polymerization were observed by MALDI-TOF mass spectrometry.

**Figure 6.** AFM images indicate that the HBFP serves as an excellent material for application in imprint lithography.

**2) Statement of the problem studied.**

Improved understanding of the structural conformation, three-dimensional solid-state packing, and physical and mechanical properties of highly-branched polymers was gained, and then used for the development of highly specialized materials. Specifically, the objective was the creation of globular molecules that would exhibit extremely low friction properties, and thus perform as "self-lubricated molecular ball bearings". Therefore, dendritic (tree-like) and hyperbranched fluoropolymers were designed to possess very low surface energies and exhibit minimal adhesive and cohesive character. The fundamental knowledge that has been gained and the tailored materials that have been prepared can be of benefit to the U.S. Army. For example, the hyperbranched fluoropolymers are promising as barriers to the passage of chemical and biological agents, and they have demonstrated superior performance as mold release agents, which could impact all areas of stamping, imprinting, injection molding, etc.

### 3) Summary of the most important results.

#### A) Dendritic Macromolecules

##### (1) Dendrimer conformation and packing in the solid-state

A combination of selective placement of stable isotopes ( $^{13}\text{C}$  and  $^{19}\text{F}$ ) within the benzyl ether based dendritic polymer structure and rotational-echo double resonance (REDOR) NMR determination of  $^{13}\text{C}$ - $^{19}\text{F}$  coupling between  $^{13}\text{C}$  labels at the chain ends (labeled as "external" in the structure as drawn below) and a  $^{19}\text{F}$  at the focal point, allowed for the observation and quantification of the extent of intramolecular inward-folding of the chain ends and intermolecular dendrimer-dendrimer interpenetration in the solid state (Wooley, K. L., Klug, C. A., Tasaki, K., Schaefer, J. "Shapes of Dendrimers from Rotational-Echo Double-Resonance NMR", *J. Am. Chem. Soc.*, **1997**, *119*,

53). From these experiments, it was found that the chain ends of the dendrimers are not limited to the external surface of the molecule, but rather that significant extents of inward-folding occur (this should be qualified by noting that the chain ends of the dendrimers in this case are chemically compatible with the remainder of the structure). This conclusion was contradictory to the belief by many researchers in the field, but it has more recently been supported by others' experiments. In addition, it was observed that each dendrimer exists as a globular entity, which

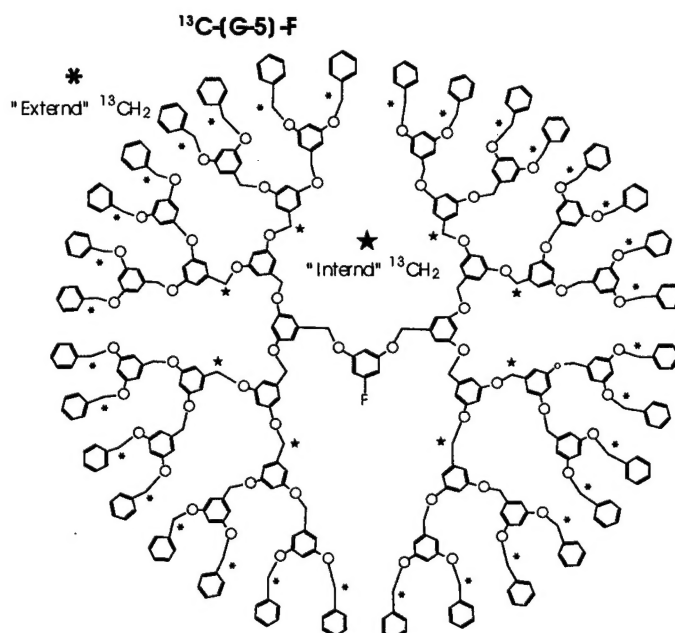


Figure 1. A fifth generation benzyl ether dendrimer, illustrating the chemical structure and the  $^{13}\text{C}$  and  $^{19}\text{F}$  labeling.

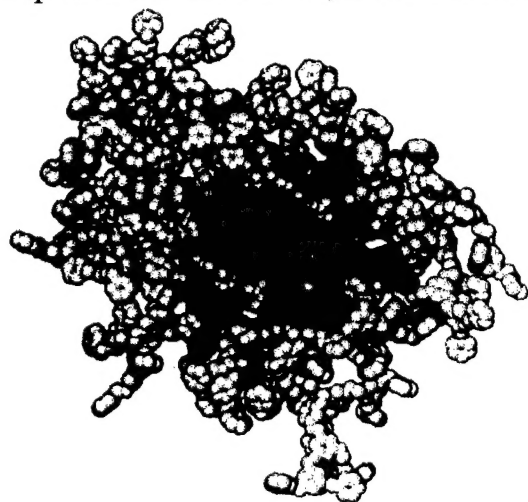


Figure 2. Molecular model of a cluster of seven fifth generation benzyl ether dendrimers, which was generated using the REDOR solid-state NMR data for intermolecular  $^{13}\text{C}$  (chain end) to  $^{19}\text{F}$  (focal point) distances.

is penetrated by the surrounding dendrimers, but no significant entanglements were found. These results agree with the physical properties that have been characterized for dendrimers over the past decade, but they are the first direct and quantitative evidence of the molecular conformation and packing.

In order to further develop a model of the conformational limitations of dendritic macromolecules, as well as their nature of packing in the solid state, benzyl ether dendrimers were prepared with  $^{13}\text{C}$  labels located within "internal" (with respect to the bonding sequence) benzylic positions and a single  $^{19}\text{F}$  label at the focal point. REDOR NMR experiments have been performed to investigate the distance constraints between the

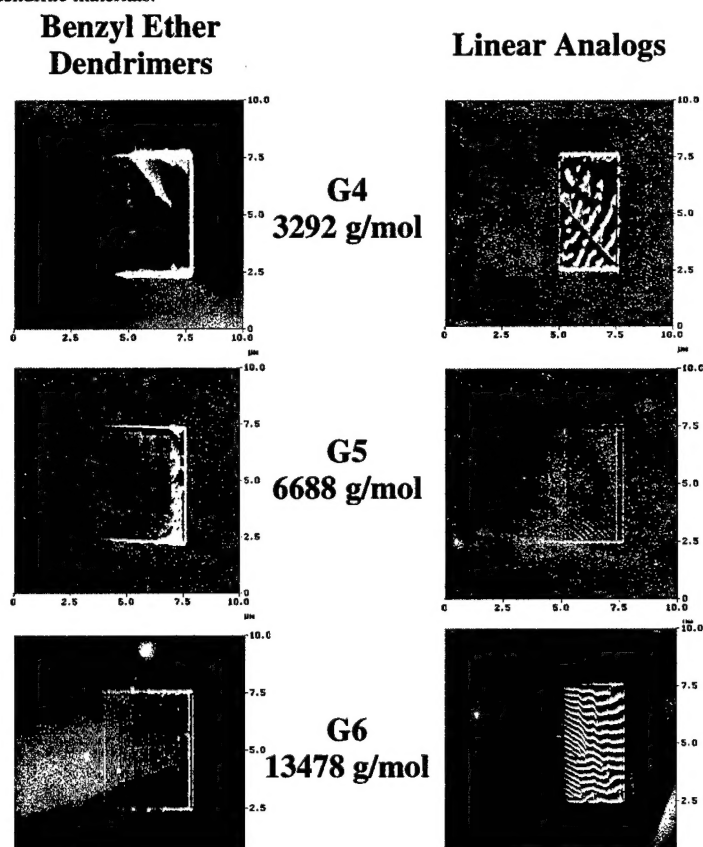
“internal”  $^{13}\text{C}$  labels and the  $^{19}\text{F}$  focal point. For the fifth generation dendrimer, it has been found that the combined intermolecular and intramolecular distances from internal  $^{13}\text{C}$  labels to  $^{19}\text{F}$  focal point are very similar to those previously measured for the external  $^{13}\text{C}$ -labeled benzyl ether dendrimer. This is a very surprising result, because it means that the external  $^{13}\text{C}$  labels, which are bonded to the  $^{19}\text{F}$  label at a more than 10 Å distance beyond the internal  $^{13}\text{C}$  labels, are further removed in three-dimensional space by only ~1 Å! These studies involved collaborative activities with Professor Jacob Schaefer (Washington University).

## (2) Physical and mechanical properties of dendrimers vs. linear analogs.

Exact compositional linear analogs to the dendritic benzyl ether macromolecules were synthesized by a one-step AB polymerization, followed by separation of different molecular weight polymers by size exclusion chromatography (this is a different approach to the stepwise synthetic route undertaken by Hawker, *et al*). Linear polymers with molecular weights equivalent to third, fourth, fifth and sixth generation dendrimers were isolated. Atomic force microscopy experiments were then developed to characterize the differences in micromechanical properties that result from different polymer architectures having the same chemical composition. As shown in the following AFM images, each dendrimer sample undergoes significant machining from the surface of ultra-thin films due to the lack of

intermolecular entanglements. In contrast, the linear polymer analogs exhibit stick-slip behavior, which is characteristic of entangled linear polymer materials. The differences in behavior can only be due to the differences in branching degree for the dendrimers (100% branched) and linear polymers (0% branched), since the effects associated with differences in composition and molecular weight were eliminated. We are now involved with developing AFM methods and data analysis routines to establish quantification of the mechanical properties of

**Figure 3.** AFM experiments reveal that the dendrimers are machined at low forces, due to the lack of intermolecular entanglements. In contrast, the linear polymer analogs (same composition and molecular weight, but 0% branching) develop periodic oscillatory patterns under the force of the scanning probe tip, resulting from stick-slip behavior that is characteristic of entangled polymer chains. These differences in behavior are expected to have implications toward the solid-state applications of dendritic materials.

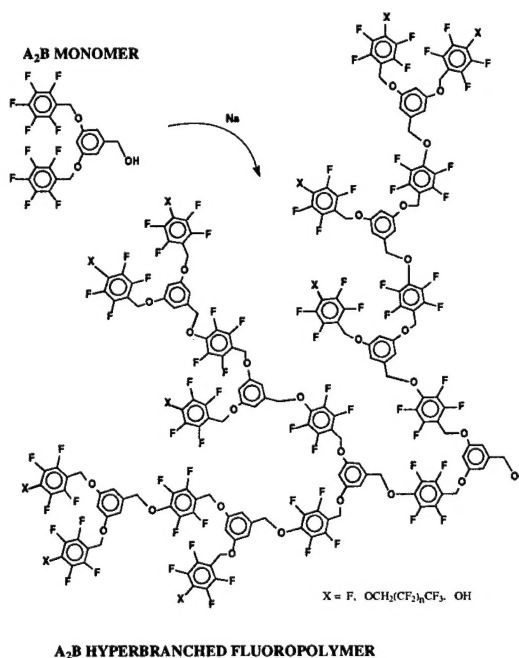


materials. This work has been accomplished in collaboration with Professor Tomasz Kowalewski (Department of Chemistry, Washington University). [Fields, H. R. Jr.; Kowalewski, T.; Schaefer, J.; Wooley, K. L. "AFM Investigation of Micromechanical Properties of Poly(benzyl ether) Dendrimers and Their Linear Analogs", *ACS Polym. Prepr.* **1998**, 39(2), 1169. Fields, H. R.; Kowalewski, T.; Schaefer, J.; Wooley, K. L. "Synthesis and Micro-mechanical Characterization of Linear Polymer Analogs to Poly(benzyl ether) Dendrimers", *ACS Polym. Prepr.*, **1998**, 39(1), 333.].

## B) Hyperbranched Fluoropolymers

### (1) $A_2B$ polymerization, chemical modification and crosslinking

The structural information gained and the properties observed, as described above, then allowed for the preparation of "self-lubricating molecular ball bearings". It was determined that the incorporation of fluorocarbon units into the dendritic structure could impart a further reduction in the cohesion of the materials by a reduction in the intermolecular attractive forces, which would enhance the effects from the lack of intermolecular entanglements. Several dendritic macromolecules were prepared, but then a hyperbranching polymerization scheme (to yield polymers containing branching sites at approximately 50% of the repeat units) was adopted to readily provide for large quantities of material. The polymerization of the  $A_2B$  monomer shown in Figure 4 is accomplished by nucleophilic aromatic substitution, using sodium to deprotonate the benzylic alcohol position and facilitate the reaction. The molecular weights are controllable between a few hundred and a few hundred thousand Daltons. Modification of the chain ends after polymerization is possible through nucleophilic aromatic substitution of the remaining pentafluorophenyl groups. This polymerization has been optimized to allow for multiple tens of grams to be synthesized in a single batch, for analysis and development of potential applications as described below.



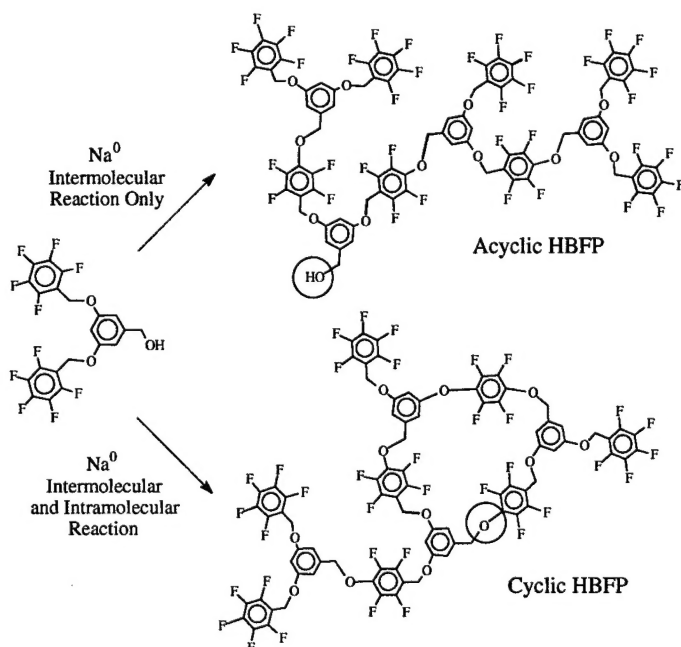
**Figure 4.** Polymerization of the  $A_2B$  monomer to yield the hyperbranched fluoropolymer. Subsequent chain end reactions allow for modification of the chain end compositions.

When 1H,1H,2H,2H-perfluorodecanoxy groups are placed at the chain ends, the material has contact angles with water and hexadecane ( $\theta_{H_2O} = 120 \pm 1^\circ$  and  $\theta_{hexadecane} = 67 \pm 3^\circ$ ) in excess of those observed for polytetrafluoroethylene (PTFE,  $\theta_{H_2O} = 115 \pm 1^\circ$  and  $\theta_{hexadecane} = 42 \pm 2^\circ$ ), indicating that the hyperbranched material has a substantially lower surface energy. This is further confirmed by AFM determination of surface friction coefficients ( $\mu = 0.028 \pm 0.003$ ) and adhesive forces ( $F_a = 38 \pm 8$  nN), which again are much improved over the values obtained for PTFE ( $\mu = 0.047 \pm 0.004$  and  $F_a = 57 \pm 4$  nN). Therefore, the



hyperbranched fluoropolymers may serve as highly-lubricating, non-interacting globular nanoparticles with repellent properties. [Mueller, A.; Kowalewski, T.; Wooley, K. L. "Synthesis, Characterization and Derivatization of Hyperbranched Polyfluorinated Polymers", *Macromolecules*, **1998**, 31(3), 776-86; Mueller, A.; Kowalewski, T.; Wooley, K. L. "Hyperbranched Perfluorinated Polymers: Surface Properties and Micromechanical Behavior", *ACS PMSE Proceedings*, **1997**, 77, 89; Mueller, A. and Wooley, K. L. "Hyperbranched Perfluorinated Polymers", *Polym. Prepr.*, **1997**, 38(1), 58].

## (2) Cyclization—understanding polymerization behavior



**Figure 5.** Intermolecular reactions produce the hyperbranched fluoropolymer (Acyclic HBFP), whereas a combination of intermolecular reactions with an intramolecular cyclization yields the cyclic HBFP. Each of the acyclic and cyclic materials at differing degrees of polymerization were observed by MALDI-TOF mass spectrometry.

The extent of cyclization that occurs during hyperbranching polymerization has long been mentioned in the literature, but only indirectly observed. Unlike linear polymerizations, which consume the two reactive chain ends upon macrocycle formation, hyperbranching polymerizations consume the unique focal point functionality and only one of the many other chain ends. As shown in Figure 5, intermolecular reactions produce the acyclic hyperbranched fluoropolymer (acyclic HBFP), whereas a combination of intermolecular and a single intramolecular reaction yields the HBFP containing a macrocycle (cyclic HBFP). Thus, the cyclic HBFP can continue to grow through reaction of the pentafluorophenyl groups, and HBFP structures at each

degree of polymerization can be either acyclic or cyclic. This makes detection of the cyclized products difficult, however, we recently accomplished the direct detection of cyclized products in the hyperbranched polymer products, by analysis with MALDI-TOF mass spectrometry. Because cyclization of the acyclic HBFP results in loss of HF (20 mass units), the acyclic and cyclic species differ by 20 mass units, which is easily detectable by MALDI-TOF analysis. The extent of cyclization varied with reaction conditions from ca. 10% to nearly 100% cyclized products vs. acyclic products being detected. This work was done in collaboration with Professor Michael Gross (Washington University). [Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. "Cyclization in Hyperbranched Polymer Syntheses: Characterization by MALDI-TOF Mass Spectrometry", *J. Am. Chem. Soc.*, **1998**, 120, 10180].

### (3) Applications

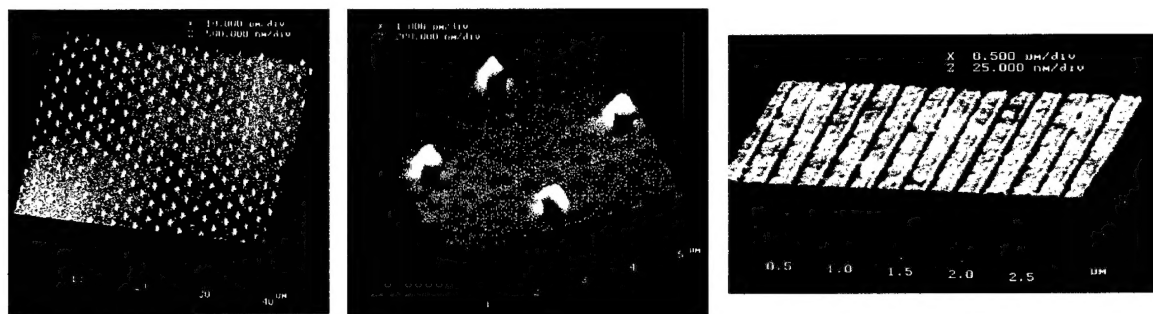


Figure 6. AFM images indicate that the HBFP serves as an excellent material for application in imprint lithography.

The above atomic force microscopy (AFM) images illustrate the excellent performance of the hyperbranched fluoropolymer material in imprint lithographic applications. The far left image shows the regularity and reproducibility of the *ca.* 250 nm (0.25  $\mu$ m) diameter punctures created in a thin film (*ca.* 100 nm thickness) of the polymer, and the center image is of higher resolution to view the size and regularity of the holes. Upon pressing the imprinter into the film at room temperature, the low  $T_g$  and lack of extensive chain entanglements, which are characteristic properties for this hyperbranched fluoropolymer, allows for it to be readily expelled from the holes, generating piles of material adjacent to the punctures. Because of the high fluorocarbon content and resulting low surface energy, the material is minimally-adhesive toward the imprinter. Additionally, narrow lines of 50-60 nm thickness and with spacings of 210 nm can be imprinted onto the surface of this polymer material (far right image). At the moment, it seems that the only limitation in the size of the features is the size of the features that can be fabricated on the imprinter. Alternatively, the hyperbranched fluoropolymer has been used as a coating on the imprinter to prevent adhesion of other polymer films during imprinting. In this application as a mold release agent, the hyperbranched fluoropolymer has performed substantially better than commercially available mold release agents. This work is being done in collaboration with Professor Robert Krchnavek (Rowan University).

#### 4) List of all publications and technical reports.

- Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. "Cyclization in Hyperbranched Polymer Syntheses: Characterization by MALDI-TOF Mass Spectrometry", *J. Am. Chem. Soc.*, **1998**, *120*, 10180.
- Straw, T. A.; Mueller, A.; Stefanescu, A. D.; Kowalewski, T.; Wooley, K. L. "The Design, Synthesis, Characterization and Derivatization of Fluorine-Containing Dendrimers and Hyperbranched Polymers", *Chapter for monograph series 'Hyper-Structured Molecules – Chemistry, Physics, and Application'*, Japan.
- Mueller, A.; Kowalewski, T.; Wooley, K. L. "Synthesis, Characterization and Derivatization of Hyperbranched Polyfluorinated Polymers", *Macromolecules*, **1998**, *31*, 776-86.
- Mueller, A.; Wooley, K. L. "Crosslinked Hyperbranched Fluoropolymer Films", *ACS Polym. Prepr.* **1998**, *39*(2), 960.

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- Mueller, A.; Kowalewski, T.; Wooley, K. L. "Synthesis, Characterization and Derivatization of Hyperbranched Polyfluorinated Polymers", *Macromolecules*, **1998**, 31(3), 776-86.
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- Bolton, D. H. and Wooley, K. L. "The Synthesis of Polycarbonates by a Silicon-assisted Alkoxy/Carbonylimidazolid Coupling Reaction", *J. Polym. Sci, Part A: Polym. Chem.* **1997**, 35, 1133.
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- Stefanescu, A. D.; Wooley, K. L. "Hyperbranched Polyfluorinated Polymers From AB<sub>4</sub> Monomers", *ACS PMSE Proceedings*, **1997**, 77, 218.
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- Bolton, D. H. and Wooley, K. L. "Synthesis and Characterization of Aromatic Hyperbranched Polycarbonates", *ACS PMSE Proceedings*, **1997**, 77, 128.
- Mueller, A. and Wooley, K. L. "Hyperbranched Perfluorinated Polymers", *Polym. Prepr.*, **1997**, 38(1), 58.

**5) List of scientific personnel supported and advanced degrees received by them.**

- Bolton, Daniel H.—graduate student, completed Ph.D. dissertation March 30, 1998, "Synthesis, Characterization and Comparison of Hyperbranched and Linear Polycarbonates", currently employed with Bayer Corporation (Pittsburgh, PA)
- Fields, Harvey R.—graduate student, 6/95 to present, expected to complete Ph.D. dissertation 8/99 (Determination of the micromechanical properties of dendritic macromolecules)
- Mueller, Anja—graduate student, completed Ph.D. dissertation August 17, 1998, "Hyperbranched Fluoropolymers: synthesis, characterization, derivatization and application", currently a postdoctoral research associate with Professor D. O'Brien, U. Arizona
- Stefanescu, Andrei—postdoctoral associate, 11/96 to 2/98 (hyperbranched fluoropolymers), Currently employed at MEMC (St. Louis, MO)
- Wooley, Karen L.—P.I.